Scale-up Optimization and Characterization of High-nickel Cathodes

ARUMUGAM MANTHIRAM
Materials Science and Engineering Program
The University of Texas at Austin

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OVERVIEW

Timeline

- Project start date: October 2016
- Project end date: September 2021
- 65 % complete

Budget

- Total project funding
  - DOE share: $50M
- Funding received in FY 2019
  - $10M
- Funding for FY 2020
  - $10M

Barriers

- Barriers
  - Energy density
  - Cycle life
  - Abuse Tolerance
- Targets
  - High-energy-density high-nickel cathodes with long cycle life and acceptable air and thermal stability

Partners

- PNNL, BNL, INL, SLAC, BU, UCSD, UW

RELEVANCE

Relevance

- Lithium-ion cells with high-energy density and long cycle life at an affordable cost can accelerate vehicle electrification

Objectives

- Develop high-energy, long-life, stable high-nickel layered cathodes
  - High-nickel layered oxides with a specific capacity of > 200 mA h g^{-1}
  - Stabilization strategies for long cycle, air, and thermal stabilities
  - Optimization strategies for compatibility with lithium-metal anode

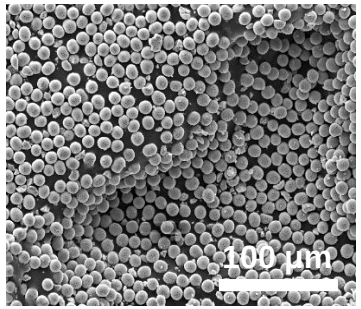
- Scale-up of high-nickel cathodes with an in-depth characterization
  - Scale-up synthesis of hydroxide precursors and lithiation processes
  - Assessment of degradation mechanisms with advanced characterization
  - Assessment of lithium-metal anode paired with high-Ni cathodes

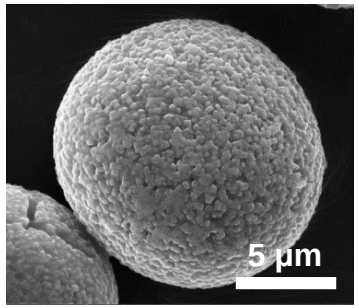
MILESTONES

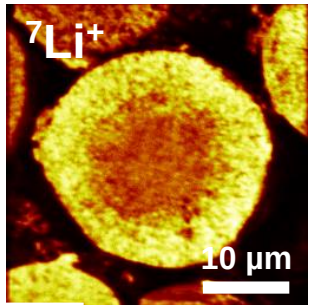
Month/Year	Milestone	Status
December 2019	Assessment of dendrite growth and surface chemistry of Li-metal anode paired with different high-Ni layered oxide cathodes	Completed
March 2020	Investigation of the current density impact on Li-metal anodes paired with optimized high-Ni layered oxide cathodes	Completed
June 2020	Investigation of lithiophilic matrices as a Li host for efficient lithium plating/stripping and Li/composite electrolyte interfaces	Ongoing
September 2020	Scale up of the hydroxide precursor (> 1 kg per batch) and lithiation (> 200 g per batch) processes of high-Ni layered oxide cathodes that are capable of delivering > 200 mA h g^{-1} with > 80% capacity retention over 200 cycles	Ongoing

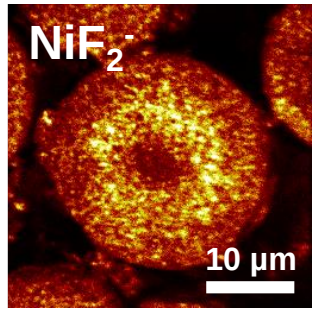
APPROACH

- **Increase energy density and reduce cost:** Increase nickel content in layered-oxide cathodes
- **Precursor scale-up**: Coprecipitation of hydroxide precursors with a tank reactor by controlling pH, temperature, and pumping rate
- **Lithiation Scale-up:** Calcination of hydroxide precursors with lithium hydroxide by controlling oxygen gas flow, temperature, and duration
- **Assessment:** Evaluation in pouch cells and characterization after extended cycling to fully understand the degradation mechanisms





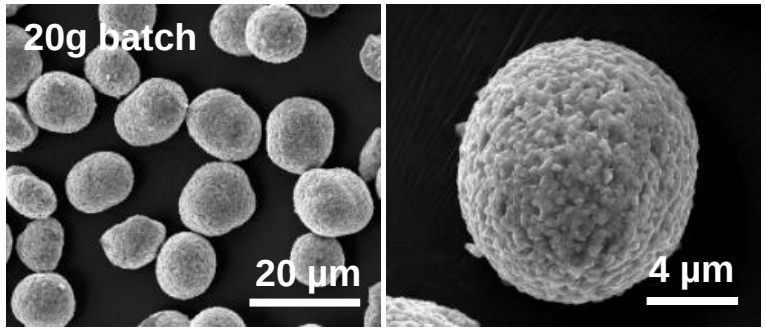


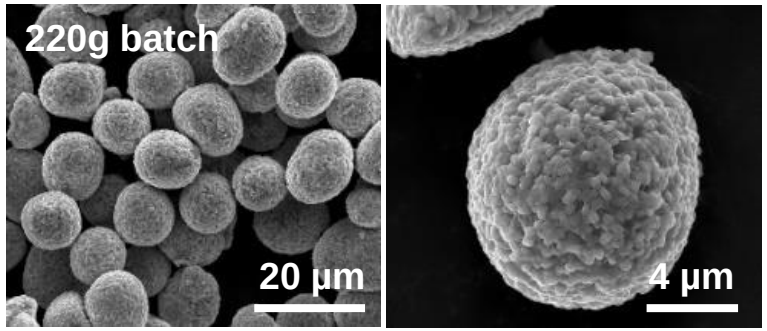


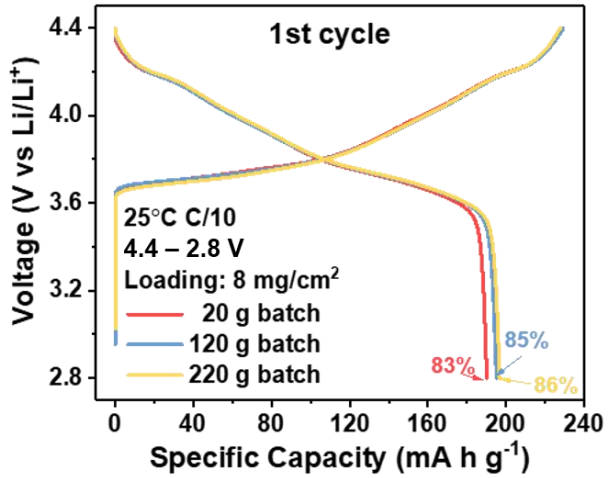
TECHNICAL ACCOMPLISHMENTS AND PROGRESS

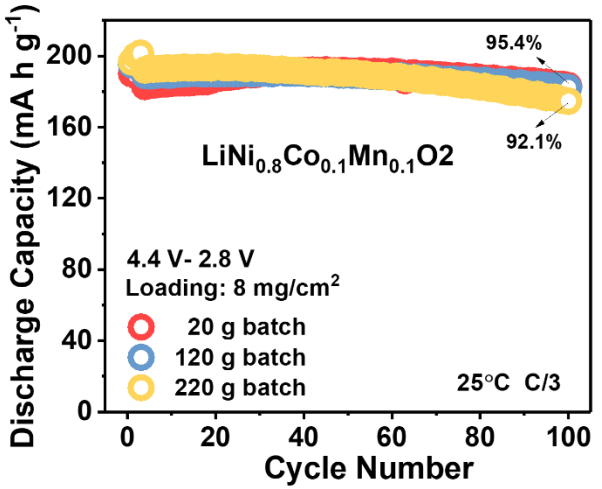
- **Scale-up:** Samples with Ni contents up to 94% have been scaled up and distributed to other team members as needed
- **Degradation mechanisms**: Major causes of degradation have been established by analyzing after extended cycling with advanced characterization methodologies
- **Stability:** Cycle life and air and thermal stability have been enhanced with appropriate doping and/or surface stabilization
- **Pairing with Li-metal anode:** A 3D lithiophilic framework has been developed as an efficient host for Li and paired with high-Ni cathodes
- **Chemical crossover:** Crossover between high-Ni cathode and Li-metal anode has begun to be explored, but hampered by limited Li cyclability

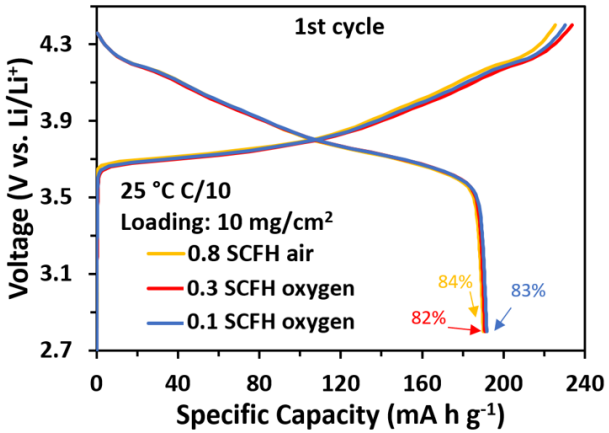
LITHIATION SCALE-UP OF $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$ (811)

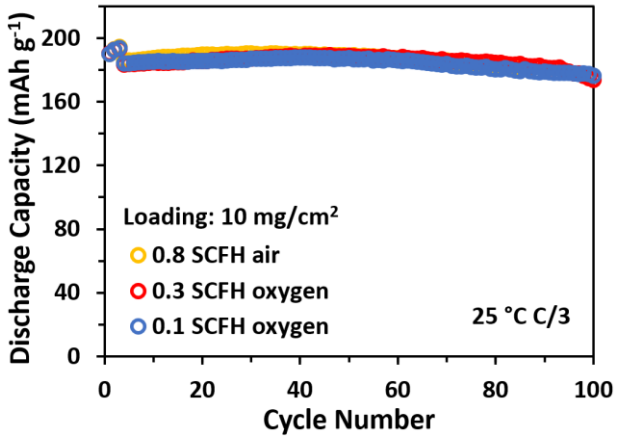






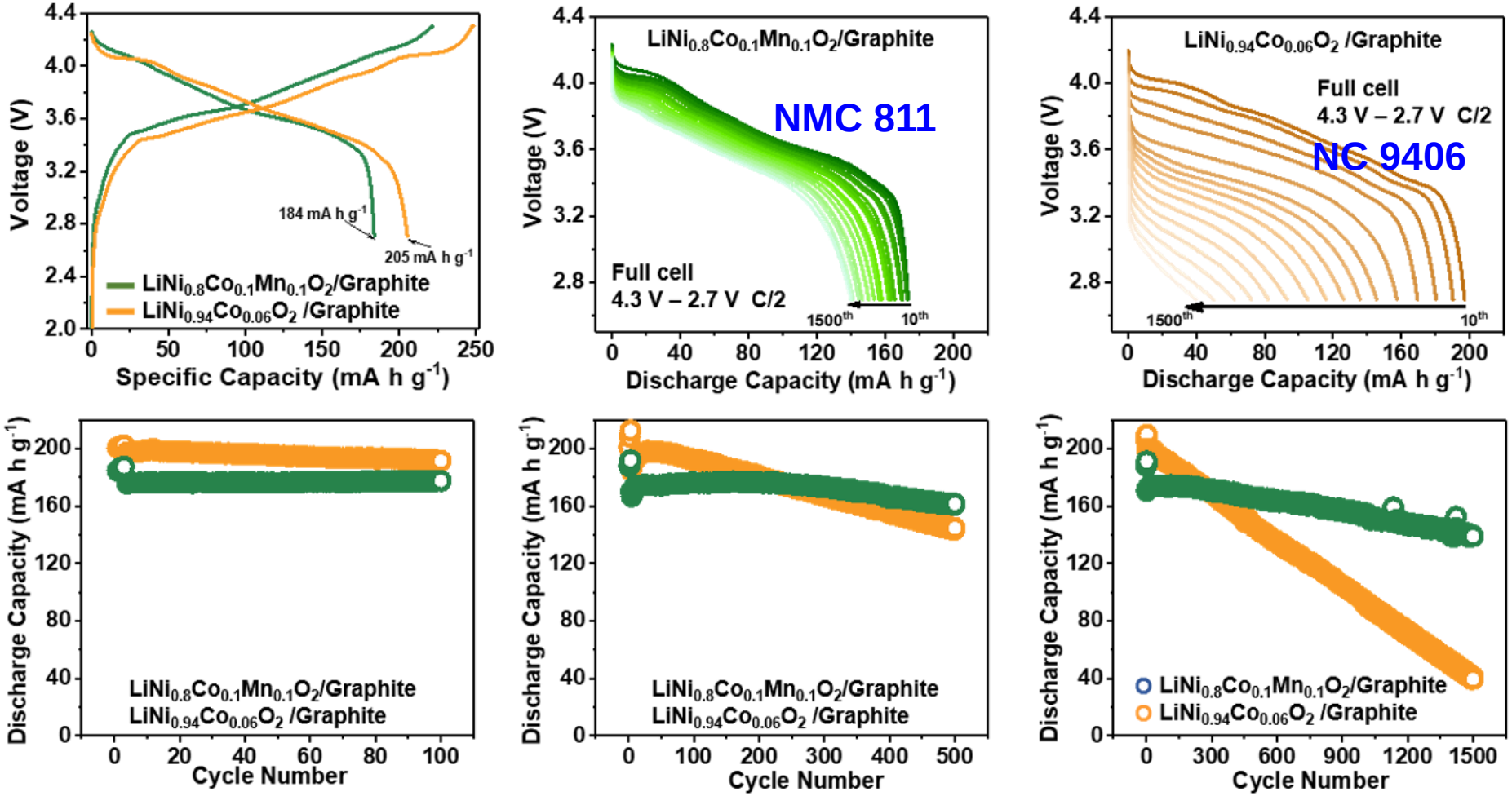






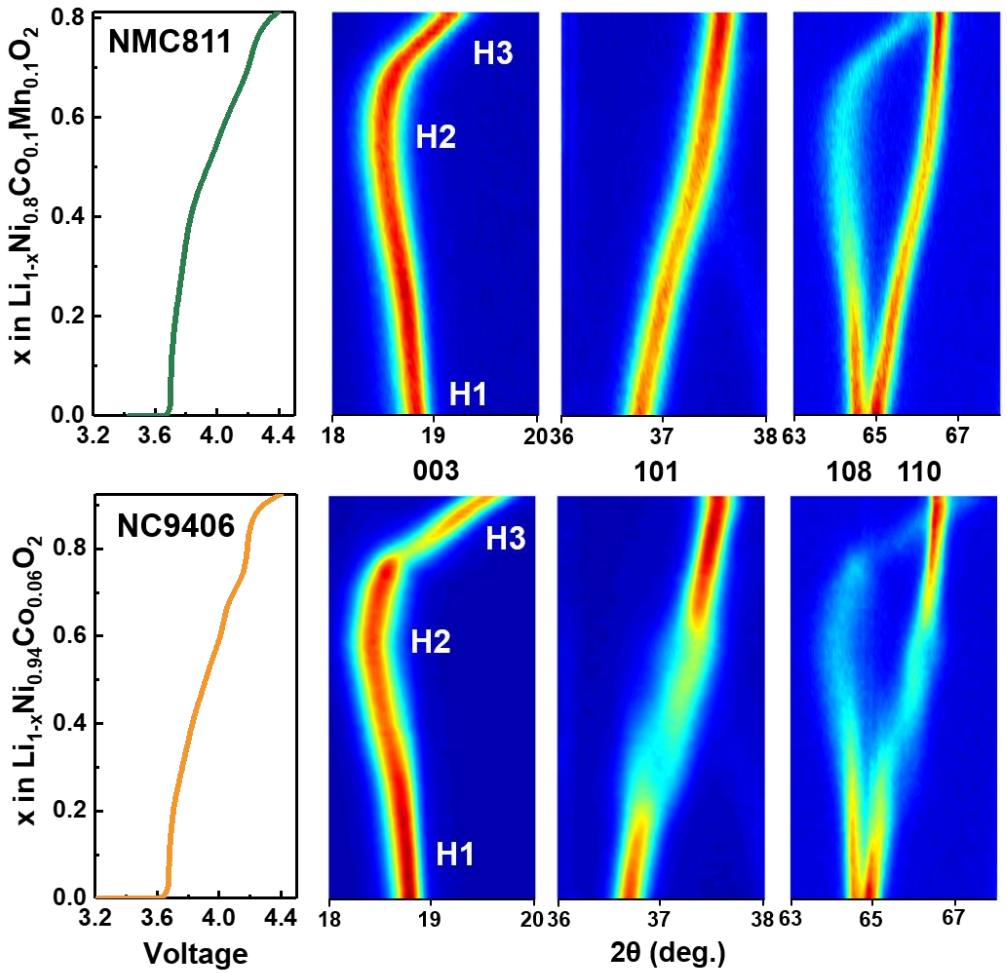
- Lithiation scaled-up (220 g) 811 exhibits performance similar to the small batch (20 g)
- Air-calcined and oxygen-calcined 811 exhibit similar cycling performances

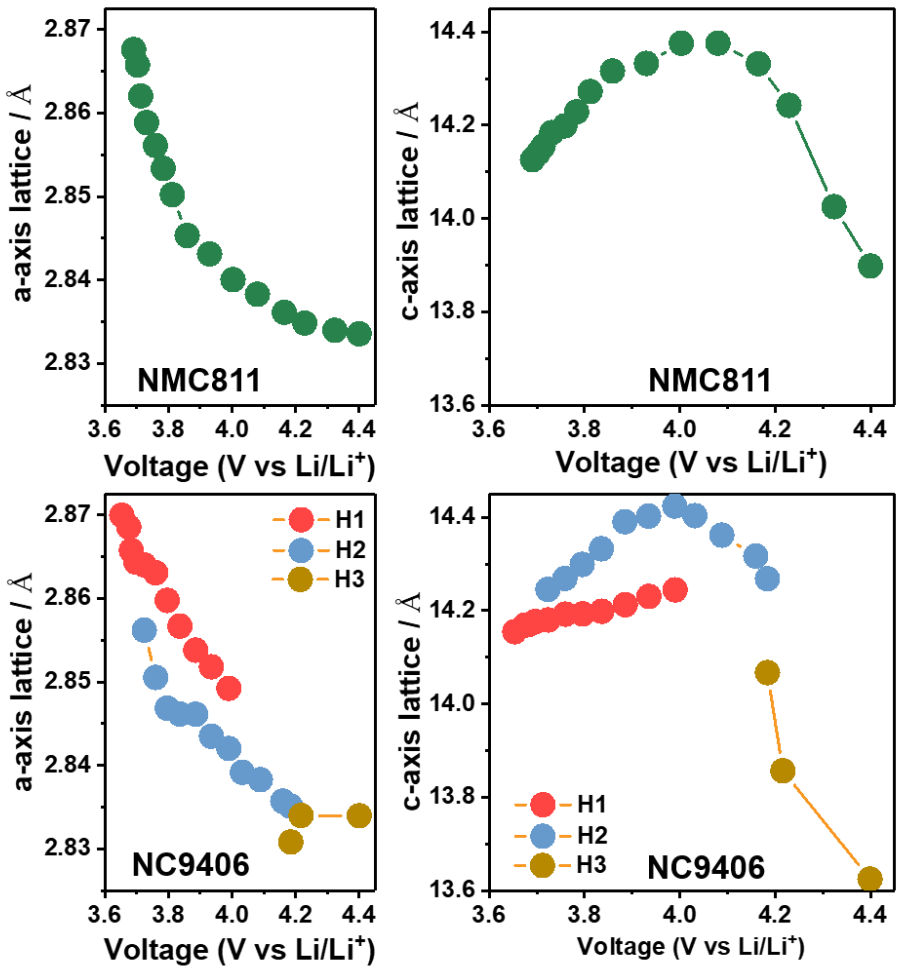
IMPACT OF NICKEL CONTENT ON CYCLE LIFE



- NC 9406 offers higher capacity, but suffers from more severe capacity fade than NMC 811, particularly at large number of cycles (*e.g.* 1,500 cycles)

IMPACT OF NICKEL CONTENT ON LATTICE STABILITY

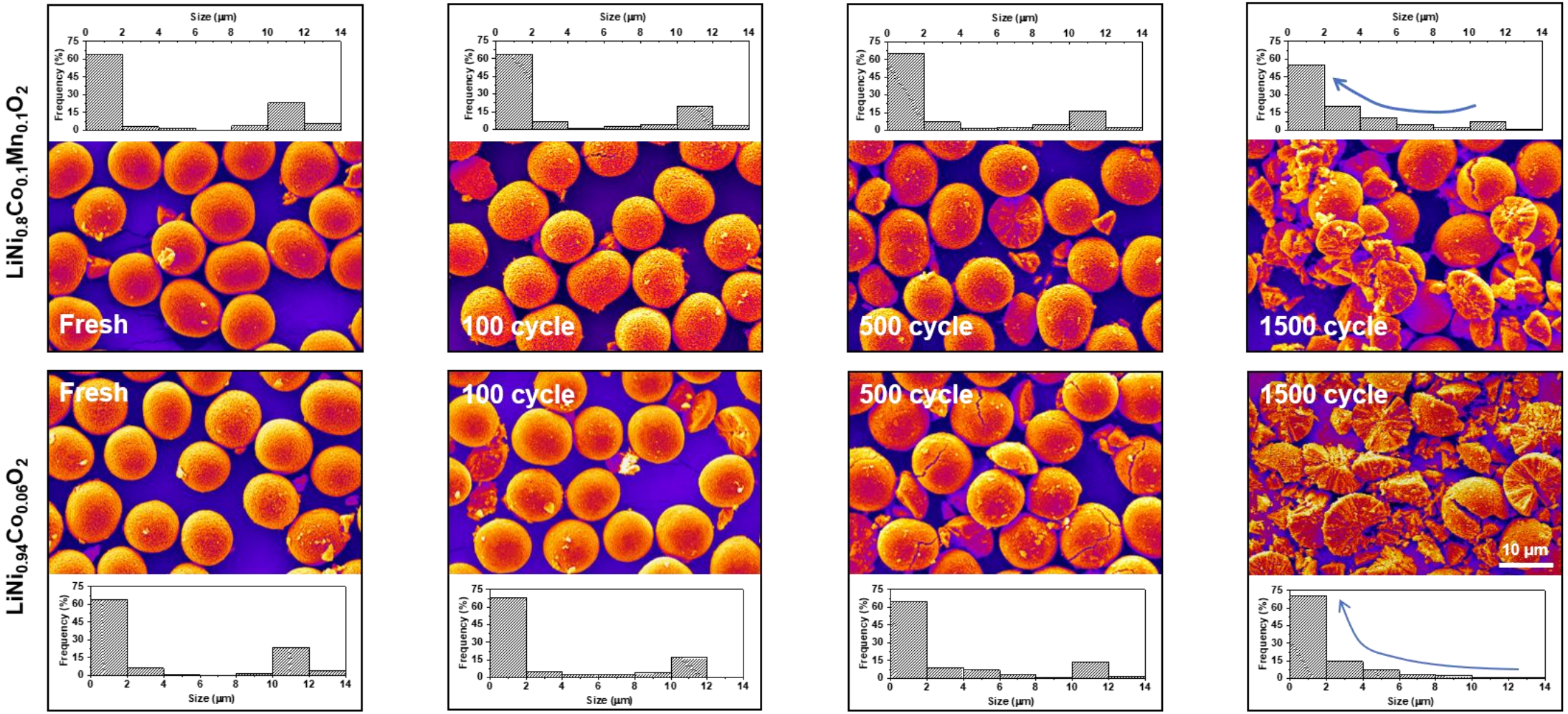




- NC 9406 suffers from more severe lattice distortion than NMC 811, resulting in structural disintegration

J. Li and A. Manthiram, *Advanced Energy Materials* **9**, 1902731 (2019)

IMPACT OF NICKEL CONTENT ON PARTICLE INTEGRITY

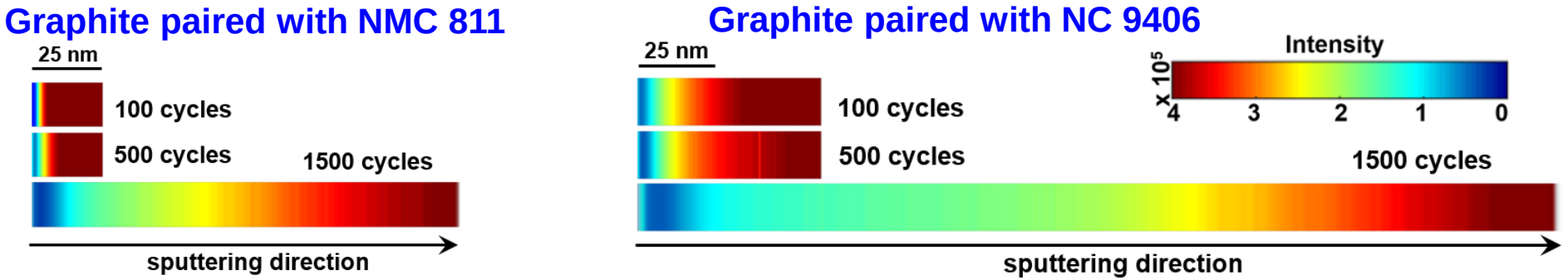


- NC 9406 shows severe cracking & pulverization at large number of cycles (1,500)

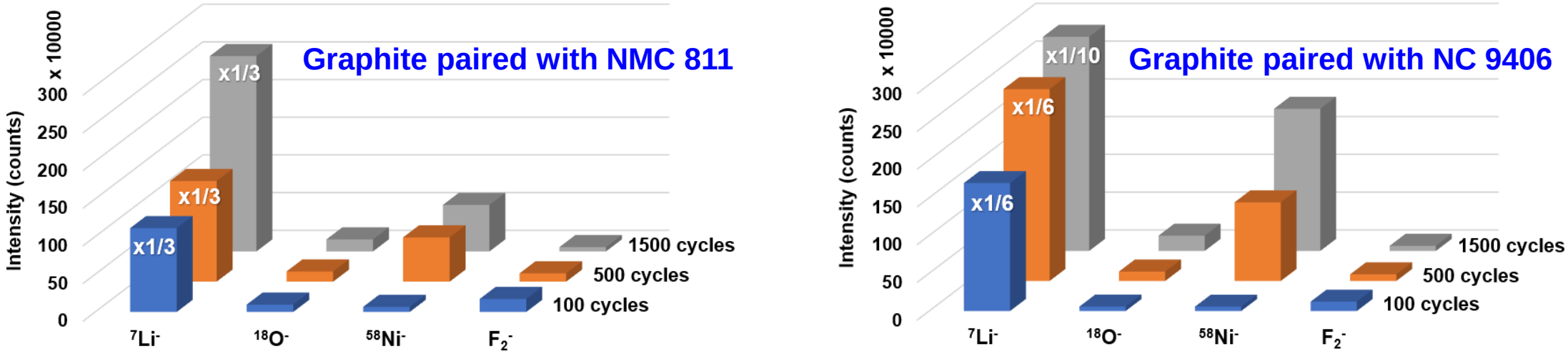
J. Li and A. Manthiram, *Advanced Energy Materials* **9**, 1902731 (2019)

IMPACT OF NICKEL CONTENT ON METAL DISSOLUTION AND SEI

Depth Profile of C_5^- fragment (representing bulk graphite)



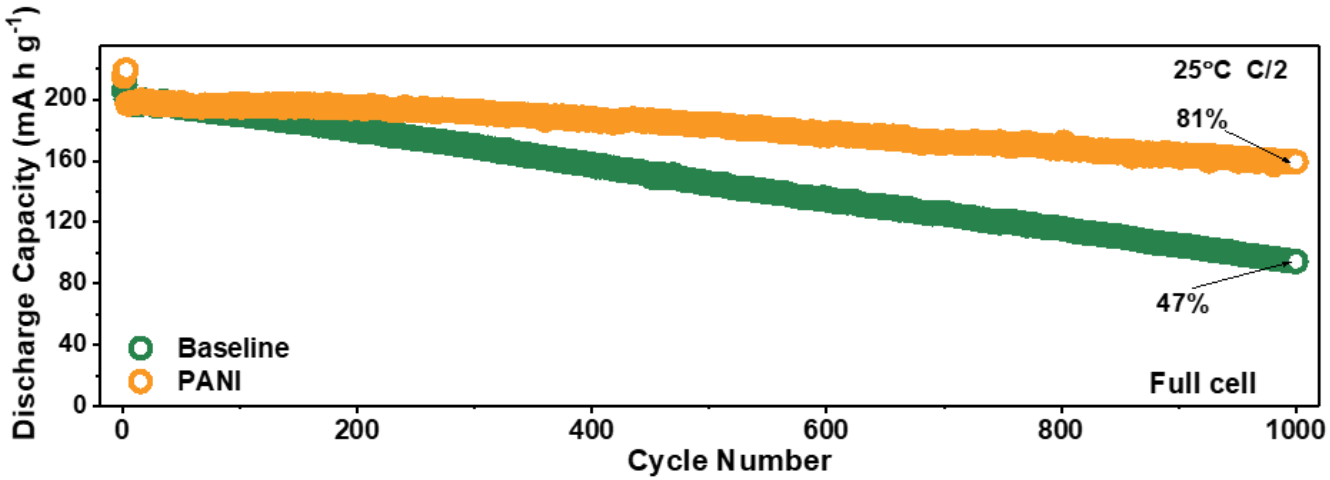
- AEI on graphite paired with NC 9406 is much thicker than that paired with NMC 811

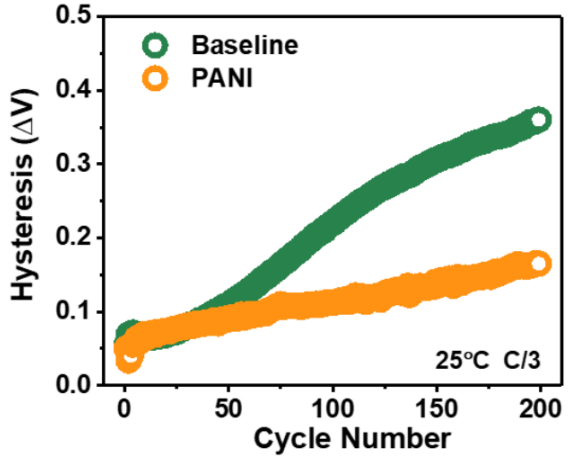


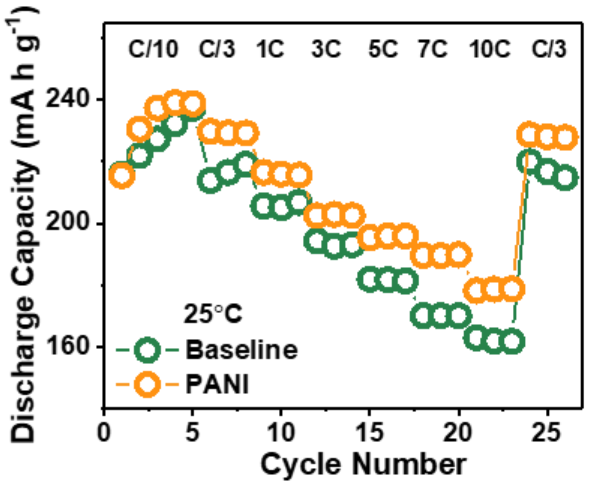
- NC 9406 exhibits more severe transition-metal dissolution and Li trapping than NMC 811

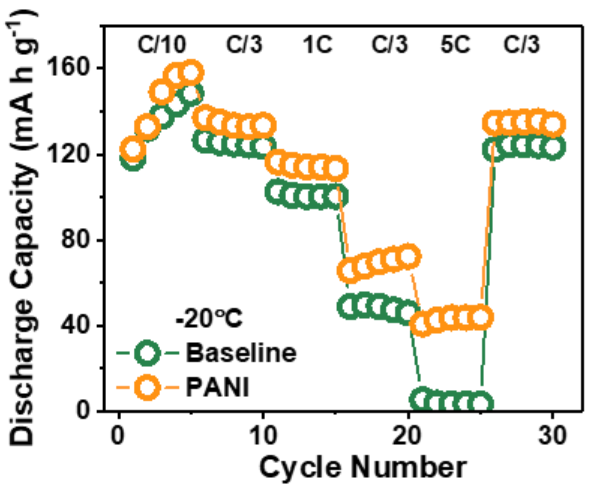
J. Li and A. Manthiram, *Advanced Energy Materials* **9**, 1902731 (2019)

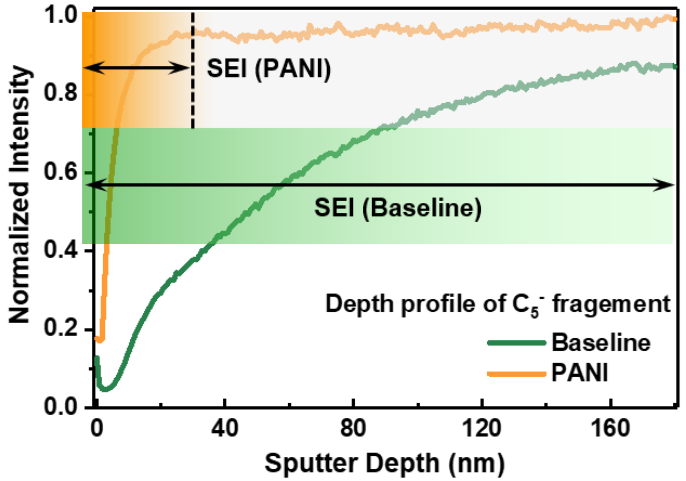
SURFACE STABILIZATION WITH POLYANILINE IN $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$







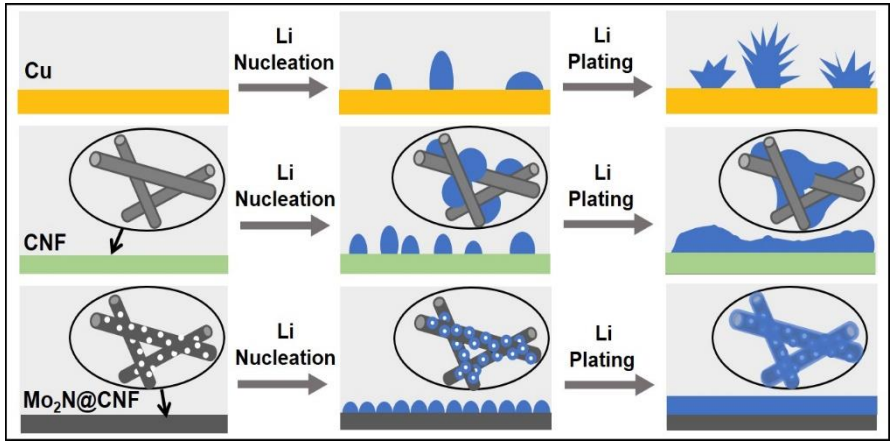


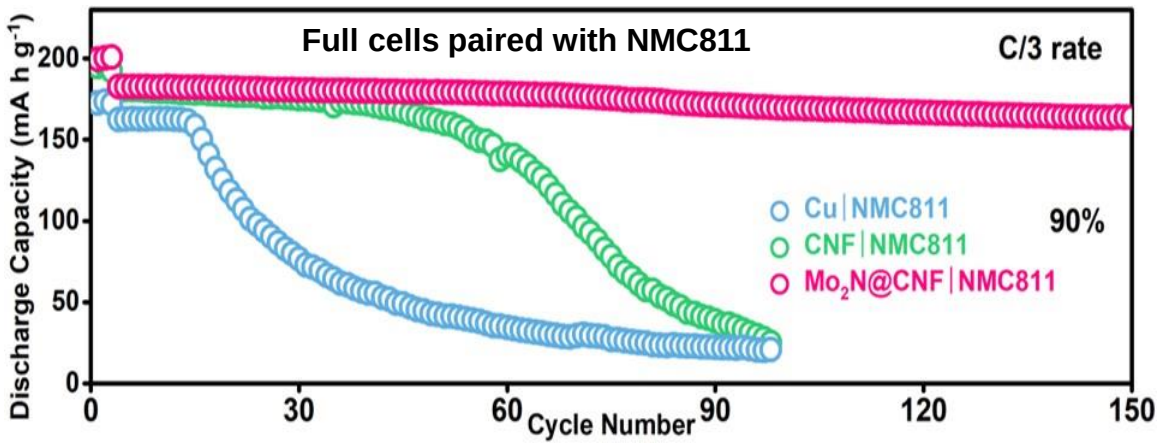


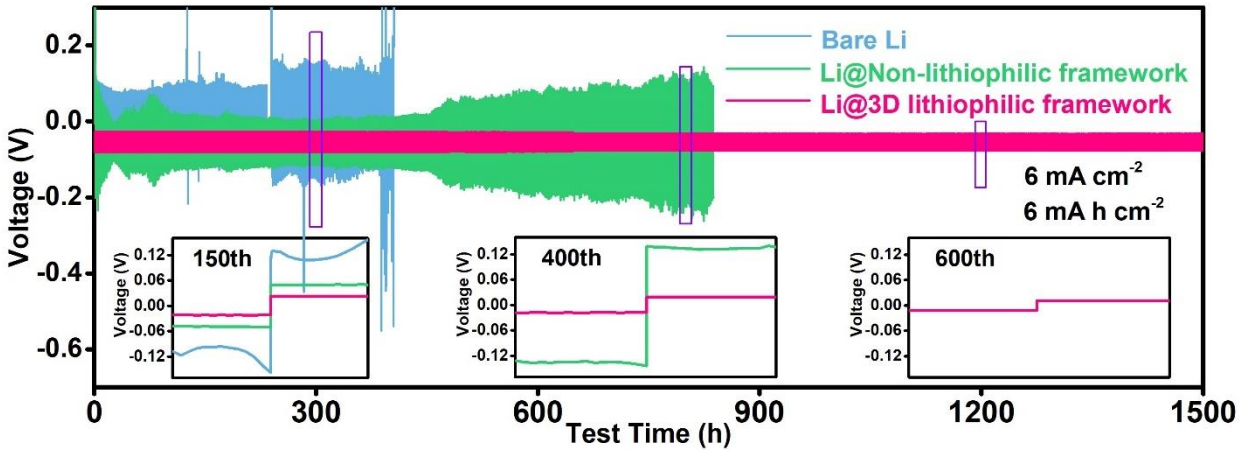
- PANI reduces surface reactivity, transition-metal dissolution, and SEI thickness on the anode (by six times), resulting in better cycle life and rate capability

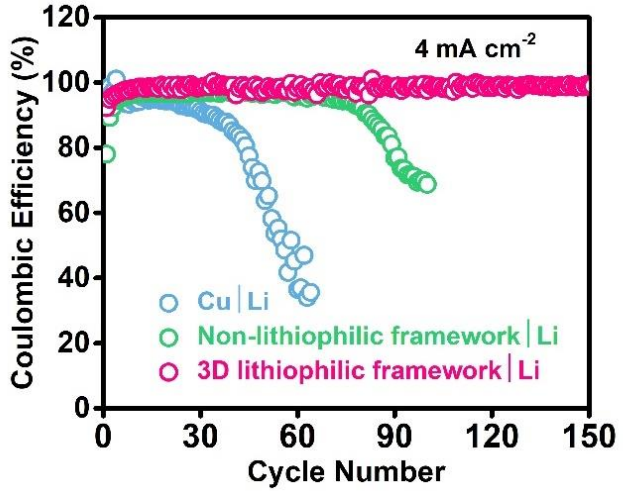
J. Li, C. H. Chang, and A. Manthiram, *Chemistry of Materials* **32**,759 (2020)

3D LITHIOPHILIC FRAMEWORK AS A Li HOST FOR 811





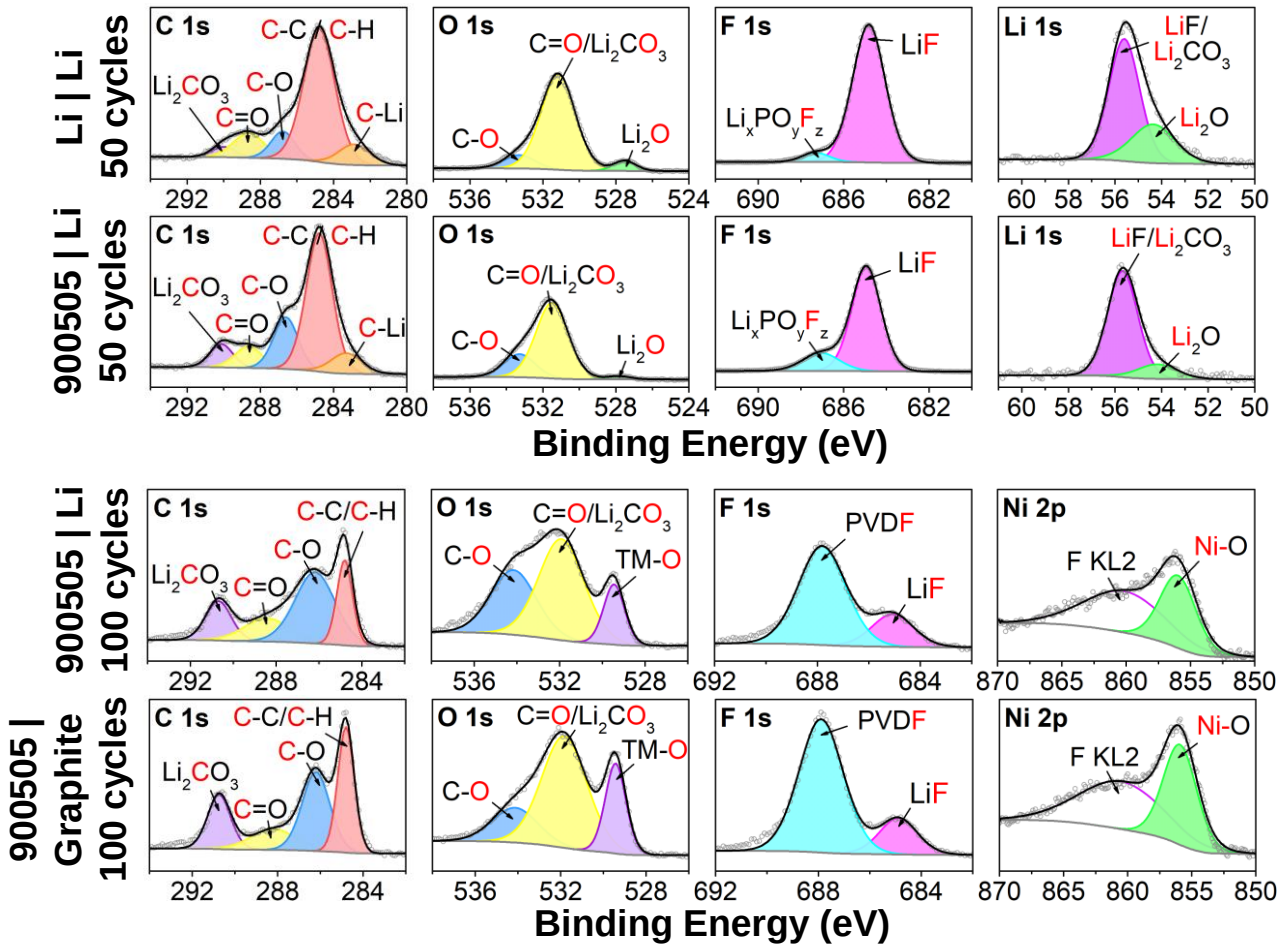


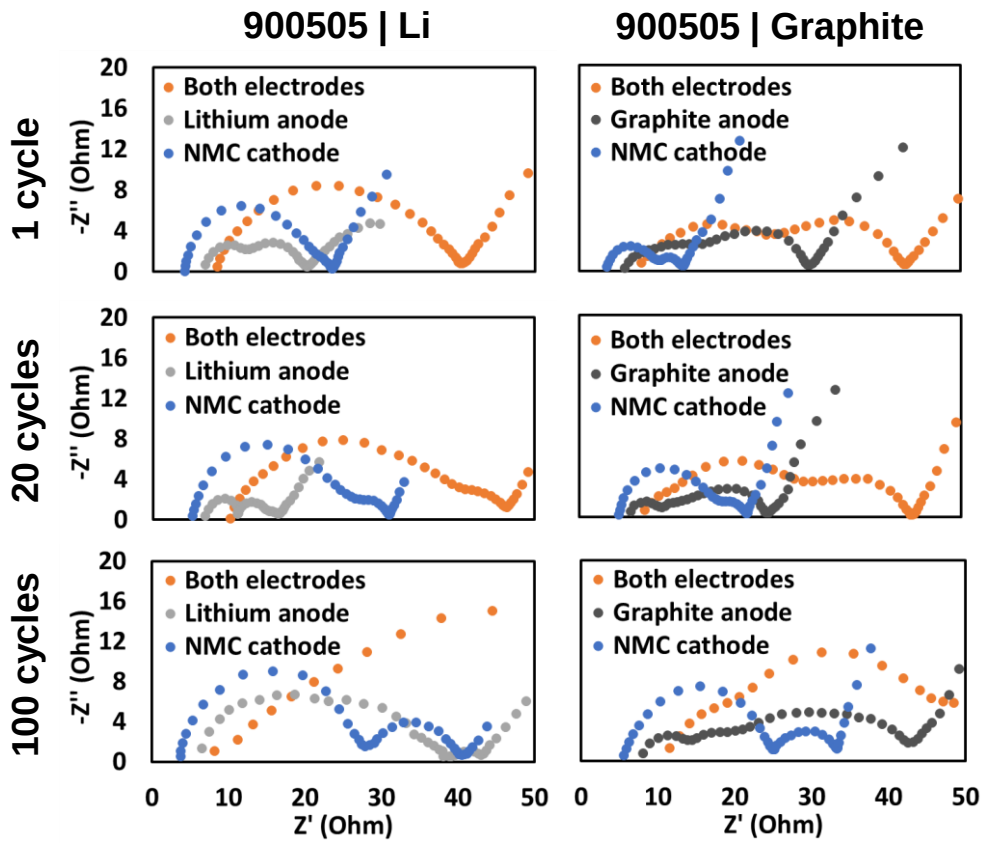


- MO_2N@CNF spatially homogenizes current distribution and lithium-ion flux with a lower overpotential, assisted by metallic Mo serving as a nucleation site for Li

L. Luo, J. Li, H. Yaghoobnejad Asl, and A. Manthiram, *Advanced Materials* **31**, 1904537: 1 - 9 (2019).

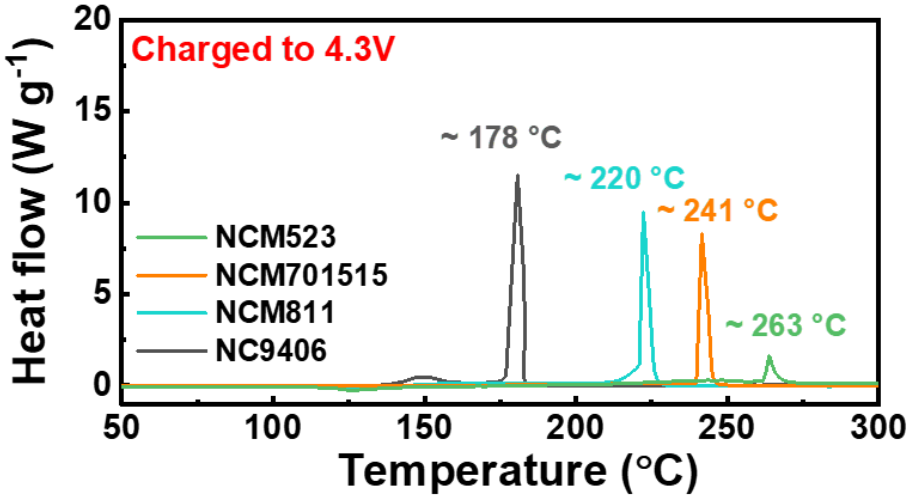
CROSSOVER EFFECTS IN LITHIUM-METAL BATTERIES

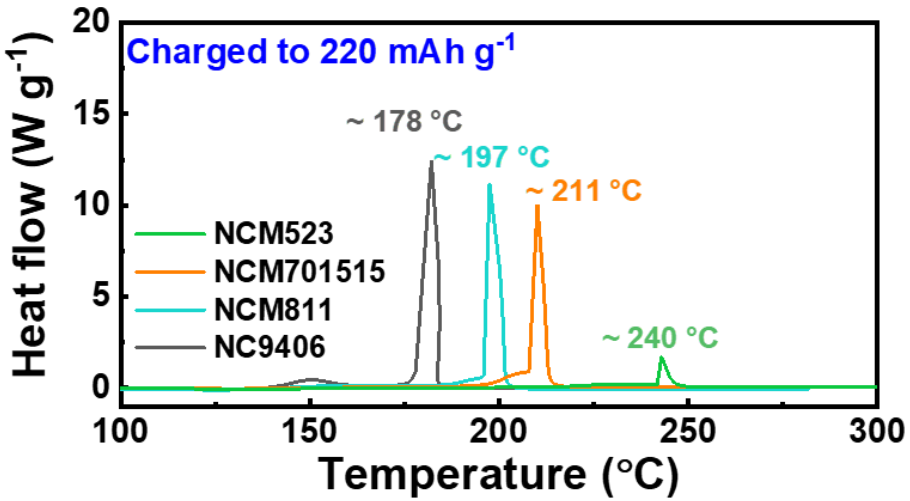


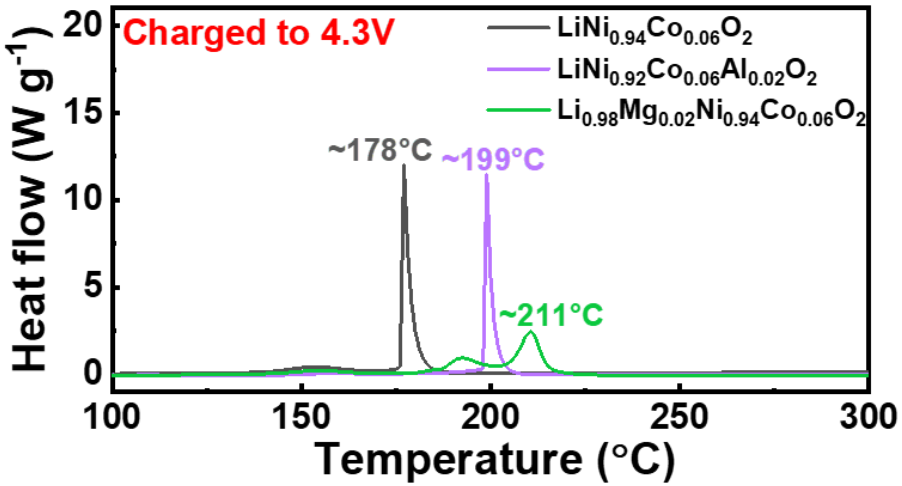


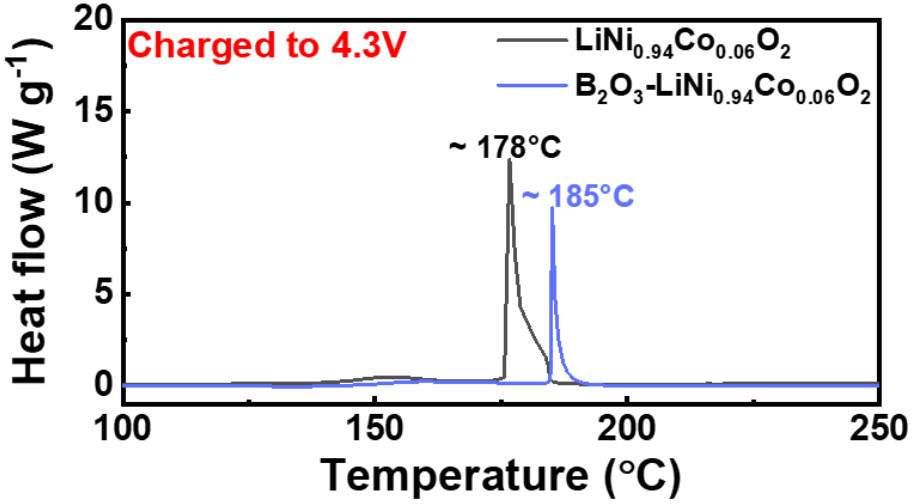
- Similar SEI on Li metal paired with Li or NMC due to limited cycle life of Li anode
- NMC paired with Li-metal anode has thicker SEI and much higher impedance even after one cycle than that paired with graphite

THERMAL STABILITY OF HIGH-NICKEL CATHODES









- Thermal stability decreases with increasing Ni content, but both thermal stability and air stability can be improved with appropriate doping and surface stabilization

RESPONSE TO REVIEWERS' COMMENTS

No presentation was given in the previous year

COLLABORATION AND COORDINATION WITH OTHER INSTITUTIONS

- Peter Khalifah and Xiao-Qing Yang, Brookhaven National Laboratory
  Structural and morphological characterization of a series of high-nickel NMCs
  - Synchrotron X-ray scattering, neutron scattering, and electron microscopy
- Stanley Whittingham at Binghamton University
  Thermal stability assessment of a series of high-nickel NMCs
- Bor Yann Liaw, Idaho National Laboratory
  In-depth electrochemical analysis of NMC 811 with different particle sizes
- Wu Xu, Pacific Northwest National Laboratory
  Evaluation of NC 9406 with different electrolyte compositions
- Ping Liu, University of California at San Diego
  Effect of secondary particle size on electrode architecture (NMC701515)
- Jihui Yang, University of Washington at Seattle
  Structural characterization of Al-doped NC9406 with *in-situ* X-ray scattering

REMAINING CHALLENGES AND BARRIERS

- **Challenge/Barrier 1:** Although the transition-metal hydroxide precursor can be obtained in 2 kg batches, the lithiation process with optimal oxygen gas flow and calcination temperature and duration remains a challenge to scale up, especially for a university lab
- **Challenge/Barrier 2:** The exponential decline in cyclability, thermal stability, and air stability with nickel contents above 80 % requires a judicious control of the cathode with doping and surface stabilization along with electrolytes compatible with both the cathode and lithium-metal anode
- **Challenge/Barrier 3:** The limited cycle life of lithium-metal anodes hampers a comprehensive analysis of the impact of cathode nickel content on the lithium-metal anode and its comparison with the well-established graphite anode

PROPOSED FUTURE WORK

- **FY2020**
  - Assess the impact of current density on Li-metal anode when paired with high-nickel cathodes
  - Explore lithiophilic hosts for Li-metal anode for enhancing the efficiency and cycle stability of Li metal and pair with high-nickel cathodes
  - Enhance the cycle life of cells assembled with Li-metal anode and high-nickel cathodes with electrolyte additives
- **FY2021**
  - Fabricate anode-free cells with high-nickel cathodes and assess Li-metal cycling efficiency to have a better understanding of the dynamics
  - Utilize the understanding gained to improve the cycle life with appropriate additives or cell engineering

Any proposed future work is subject to change based on funding levels

SUMMARY

- Scale-up of transition-metal hydroxide precursors (2 kg per batch) and lithiation process (200 g per batch) has been demonstrated
  - high-quality samples with consistent particle size, morphology, and performance
- The exponential effect of increasing nickel content from 80% to 94% has been illustrated by comparing NMC 811 and NC 9406
  - rapid capacity fade due to phase transition, cracking, transition-metal dissolution and crossover, and thick SEI formation and Li trapping at anode
- Surface stabilization with polyaniline improves performance
  - improves cyclability and rate capability due a reduction in transition-metal dissolution, crossover to anode, and SEI thickness on the anode
- 3D lithiophilic hosts for Li metal offer longer cycle life with NMC cathodes
- Effect of transition-metal crossover on Li metal could not be established due to limited cycle life, but crossover from Li-metal anode seems to impact the cathode
- Thermal stability decreases with Ni content, but doping helps to improve it